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Cyclic trimeric and high polymeric phosphazenes bearing cinnamate groups were synthesized and characterized. Cyclic trimers with the general formula $N_3P_3R_yR'_x$, where $R=OC_6H_4OC(O)CH=CHPh$, $R'=OCH_2CF_3$ (y=1, x=5 and y=6, x=0), and $R=(OCH_2CH_2)_2OC(O)CH=CHPh$ (y=1, x=5 and y=6, x=0) were synthesized. Also synthesized were high polymeric phosphazenes $[NPR_xR'_y]_n$, where $R=OC_6H_4OC(O)CH=CHPh$, $R'=OCH_2CF_3$ (y=x=1 and y=0, x=2) and $R=(OCH_2CH_2)_2OC(O)CH=CHPh$ (y=x=1 and y=0, x=2). The photo-cross-linking of a representative polymer was studied by UV spectroscopy.

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Technical Report No. 21

THE SYNTHESIS AND CHARACTERIZATION OF SMALL MOLECULE AND PHOTO-CROSS-LINKABLE HIGH POLYMERIC PHOSPHAZENES BEARING CINNAMATE GROUPS

by

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Prepared for Publication in *Macromolecules*

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Abstract

Cyclic trimeric and high polymeric phosphazenes bearing cinnamate groups were synthesized and characterized. Cyclic trimers with the general formula $N_3P_3R_yR'_x$, where $R=OC_6H_4OC(O)CH=CHPh$, $R'=OCH_2CF_3$ (y=1, x=5 and y=6, x=0), and $R=(OCH_2CH_2)_2OC(O)CH=CHPh$ (y=1, x=5 and y=6, x=0) were synthesized. Also synthesized were high polymeric phosphazenes $[NPR_xR'_y]_n$, where $R=OC_6H_4OC(O)CH=CHPh$, $R'=OCH_2CF_3$ (y=x=1 and y=0, x=2) and $R=(OCH_2CH_2)_2OC(O)CH=CHPh$ (y=x=1 and y=0, x=2). The photo-cross-linking of a representative polymer was studied by UV spectroscopy.

Introduction

Photo-cross-linkable polymers (photopolymers) are widely used in the fields of macro- and microlithography,[1] chemically-resistant coatings, and in the field of non-linear optical (NLO) materials.[2,3] The field of photopolymers is evolving continuously and a variety of photoactive groups (cinnamate and cinnamylidene esters, chalcone) are currently being used or investigated for cross-linking applications.

The best-known photosensitive moiety is the cinnamate group, which cross-links in a controlled 2+2 photo-induced cycloaddition. It is the cross-linking unit used in polymers for offset printing plates and microcomponents. Indeed, polymeric materials that incorporate the cinnamate group have existed since 1948.[4,5] The synthetic route to poly(vinyl cinnamate), in which poly(vinyl alcohol) is esterified with cinnamoyl chloride, serves as a model for the synthesis of a wide variety of photopolymers. Photopolymers that utilize acrylate,[6] siloxane[7-9] and vinyl[4,5] backbones have also been synthesized. While the phosphazene backbone has been used in the field of UV-cross-linkable materials,[10-14] the use of a polyphosphazene backbone as a platform for photo-cross-linkable cinnamate side groups has not yet been reported.

The use of the phosphazene skeletal system has several advantages for photopolymer applications. These are: (1) The potential cross-link density and sensitivity to UV irradiation is greater than in classical organic-backbone polymers due to the presence of two photo-cross-linkable groups per repeat unit. (2) The ability to incorporate a wide variety of cosubstituents via macromolecular substitution in polyphosphazenes allows such properties as the glass transition and the solubility to be tailored at will. (3) The absence of an absorption of the polyphosphazene backbone in the mid-UV to the near infrared region minimizes photoinduced reactions of the skeletal system during UV irradiation required for the photo-cross-linking procedure.

Results and Discussion

Synthesis and Characterization of Cyclic Phosphazene Model Compounds. The synthetic routes to the cyclic trimeric phosphazenes used as reaction models for the high polymers are shown in Schemes 1 and 2. The primary model system was simplified by use of monofunctional cyclotriphosphazenes. Hexasubstituted cyclic trimers 12 and 15 were used to model high polymers 23 and 26 in which each phosphorous atom bears two photoactive groups.

Trimers 5 and 9 were synthesized in a manner similar to each other (see Schemes 1 and 2). Hexachlorocyclotriphosphazene was first treated with either $NaOC_6H_4$-p-OBz or $NaO(CH_2CH_2O)_2THP$[15] (THP = tetrahydropyranyl) to yield the pentachloro derivitive 2 or 6. The remaining five chlorine atoms per molecule were then replaced by treatment with $NaOCH_2CF_3$ to yield the fully substituted trimers 3 and 7. Trimer 3 was deprotected to the free alcohol $N_3P_3(OCH_2CF_3)_5O(CH_2CH_2O)_2H$ (4) with the use of PPTS[16] (pyridinium-p-toluene sulfonate) in 95% ethanol. Trimer 7 required the use of iodotrimethylsilane[17] followed by hydrolysis of the resulting trimethylsilyl aryl ether with methanol to yield the free alcohol $N_3P_3(OCH_2CF_3)_5OC_6H_4OH$. Both trimers were esterified in pyridine solution with a slight excess of cinnamoyl chloride overnight at room temperature to yield cinnamate-substituted trimers 5 and 9.

Schemes 1 and 2 Near Here

However, the fully substituted trimers 12 and 15 required slightly different synthetic routes due to the nature and steric bulk of the side groups. Trimer 10 was synthesized from hexachlorocyclotriphosphazene (1) and eight equivalents of $NaOC_6H_4$-p-OBz. This species was deprotected with BBr_3[18,19] to yield the hexahydroxy compound $[NP(OC_6H_4\text{-p-}OH)_2]_3$ (11), which was esterified with cinnamoyl chloride as described above.

Trimer 13 was synthesized in a manner analogous to trimer 10. Deprotection to yield the hexahydroxy compound 14 was accomplished with the use of HCl in ethanol to cleave the

tetrahydropyranyl ether and give the trimer $[NP(O(CH_2CH_2O)_2H)_2]_3$. This trimer was esterified as described above to give $[NP(O(CH_2CH_2O)_2C(O)CH{=}CHC_6H_5)_2]_3$ (**15**).

Synthesis and Characterization of High Polymeric Phosphazenes. The synthetic pathways to polymers **20** and **24** are depicted in Scheme 3. Poly(dichlorophosphazene) **16** was prepared by the thermal ring opening polymerization of **1**. Trifluoroethoxy cosubstituent polymer **17** was prepared by allowing a stoichiometric deficiency of $NaOCH_2CF_3$ to react with polymer **16**. The remaining P-Cl reactive sites were replaced by the use of $NaOC_6H_4$-p-OBz to give fully substituted polymer **18** (see Scheme 3). Polymer **22** was prepared in a slightly different manner, by the addition of sodium trifluoroethoxide nucleophile last (see Scheme 4).

Schemes 3 and 4 Near Here

Single substituent polymers $[NP(OC_6H_4OBz)_2]_n$ (**28**) and $[NP(O(CH_2CH_2O)_2THP)_2]_n$ (**25**) were synthesized by the reaction of macromolecular intermediate **16** with $NaOC_6H_4$-p-OBz and $NaO(CH_2CH_2O)_2THP$.

Polymers **22** and **25**, bearing the THP ether protecting group, were deprotected to the free hydroxyl polymers **23** and **26**, respectively, with the use of PPTS in 95% ethanol solution.

The initial reagent explored to bring about the cleavage of the benzylic ether to obtain hydroxy-substituted polymers[20,21] was BBr_3. In both homopolymer **28** and trifluoroethoxy cosubstituent polymer **18**, BBr_3 afforded nearly complete deprotection to the free hydroxy group to give polymers **29** and **19**. However, the conditions (30 minutes with a slight excess of BBr_3 at room temperature) resulted a noticable molecular weight decline, especially with trifluoroethoxy cosubstituent polymer **18**, as estimated by the viscosity of THF solutions. Similar results were obtained when the trifluoroethoxy cosubstituent polymer was deprotected for five minutes at room temperature. It is speculated that the molecular weight decline results from the lone pair electrons on the backbone nitrogen atoms coordinating to the boron atom and leading to backbone scission.

Therefore, the use of B-Bromo-9-BBN[22] (9-bromo-9-borabicyclo[3.3.1]nonane), a milder and much more sterically hindered reagent for the cleavage of benzyl ethers than BBr_3,

was attempted for the deprotection reaction. This reagent was used in the anticipation that a more sterically crowded environment would allow the deprotection reaction to occur, while retarding the lone pair coordination which may lead to backbone degradation. The level of deprotection of both the trifluoroethoxy cosubstituent polymer **18** and homopolymer **28** was so low as to be undetectable by ^1H NMR even in the presence of more than of 10 equivalents of B-Bromo-9-BBN.

The last deprotection reagent investigated was iodotrimethylsilane. This reagent provided almost full deprotection of the trifluoroethoxy cosubstituent polymer **18** without the catastrophic molecular weight degradation that occurred with the use of BBr_3. However, in contrast to the trifluoroethoxy cosubstituent polymer, homopolymer **28** was completely unaffected by iodotrimethylsilane. This may be due to the steric crowding around the reactive Si-I bond which prevents the reaction between the sterically more demanding benzyloxyphenoxy homopolymer, than in the case of the smaller trifluoroethoxy cosubstituent.

The only reagent to fully deprotect homopolymer **28** is the relatively harsh reagent BBr_3. Backbone degradation was minimized by short (five minute) reaction times rather than the initially long times (thirty minutes).

Ultraviolet Absorption Studies of Cyclic Trimers. The UV induced 2 + 2 cycloaddition reaction of cyclic trimers that bear cinnamate side groups was investigated by the irradiation of trimer **5** with a medium-pressure Hg lamp (see Scheme 5). Trimer **5** had an absorption at 280 nm (CH_2Cl_2 solvent). Species **5** was irradiated in the solid state for two hours 10 cm from the UV lamp, to induce the formation of dimer **31**. Dimer **31** was characterized in its impure form by ^{31}P and ^1H NMR spectroscopy, and mass spectrometry. Positive FAB mass spectrometry detected the protonated molecular ion MH^+ at 1731 mass units, which matches the mass of the expected cyclobutane-type dimer. The mass spectrum showed no evidence of open-chain (non-cyclobutane) saturated species ($M^+ = 1732$). The ^1H NMR spectrum of **31** consisted of two doublets ($J = 14$ Hz) centered at 7.0 and 6.0 ppm, which, due

to symmetry considerations, indicate the formation of dimer **31** with the phenyl groups in the *Z* configuration about the cyclobutane ring.

Scheme 5 Near Here

Ultraviolet Absorption of Polymers 27 and 30. The ultraviolet absorption behavior of polymers **27** and **30** was investigated by UV spectroscopy. Thin films of polymers **27** and **30** were cast onto quartz plates from inhibitor-free THF and the solvent was removed under vacuum. The λ_{max} due the cinnamate chromophore of both polymer **27** and polymer **30** was found to be at 276 nm which compares favorably to other similar aliphatic cinnamate esters.

Photolytic Cross-linking Behavior of Polymers 27 and 30. The photolytic cross-linking of polymer **27** was followed by UV spectroscopy (see Figure 1). The polymer film was irradiated with an unfiltered sunlamp UV source. The decrease in the 274 nm absorption was used to monitor the progress of cross-linking. The photo-cross-linking presumably occurs mainly via the formation of cyclobutane-type dimers, perhaps accompanied by various free radical cross-linking reactions. Cross-linking was confirmed by the insolubility of polymer **27** in common organic solvents after irradiation.

Figure 1 Near Here

The photolytic cross-linking of polymer **30** was also followed by UV spectroscopy (see Figure 2). As can be seen in Figure 2, the photo-cross-linking behavior and the λ_{max} of polymer **30** are essentially identical to that of polymer **27**. These results indicate a minimal influence on the cross-linking process by either the loading of the photoactive group or the type of spacer, respectively.

Figure 2 Near Here

Conclusions

The synthesis and characterization of cyclic and high polymeric cinnamate phosphazenes has been investigated. The results indicate that polymers **27** and **30** undergo a photochemically induced 2 + 2 cycloaddition reaction to form a cross-linked matrix.

The synthetic routes to phosphazene-based cinnamate photopolymers described here have some limitations. The most obvious problem is a lowering of molecular weight during the deprotection and the esterification steps. This can be avoided by the derivatization of macromolecular intermediate **16** with the photoactive chalcone group (see following paper). Lastly, an ideal photoresist has a glass transition temperature significantly above room temperature and an even higher T_g after cross-linking. Although polymer **30** has a T_g of 59 °C, and polymers **24** and **27** have T_g's of -25 and -16 °C, respectively, the photolytic cross-linking behavior of polymers **27** and **30** are very similar. This is consistent with a minimal influence of the T_g on photo-cross-linking behavior. However, the effectiveness of the cross-linking step raises the possibility that this system may be useful for the cross-linking of macromolecular surface coatings.

For these reasons, further research was directed toward the incorporation of the chalcone group into the phosphazene system rather than the cinnamate unit. The synthesis of chalcone-bearing polyphosphazenes is a one step reaction and the resultant polymers have higher glass transition temperatures than do cinnamate-bearing polyphosphazenes.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. It was recrystallized from hexane and sublimed (40 °C, 0.05 mm Hg) before use. Tetrahydrofuran and dioxane were distilled from sodium benzophenone under dry argon before use. 2,2,2-Trifluoroethanol (Halocarbon) was distilled from anhydrous barium oxide and was stored over 4Å molecular sieves. All other reagents and solvents were used as received. The

reactions were performed with the reactants under an atmosphere of dry argon using standard Schlenk line techniques. Column chromatography was carried out with the use of silica as a stationary phase with the eluents as indicated in the text. Polymer **16**, $[NPCl_2]_n$, was prepared by the standard literature procedure.[23-25]

Equipment. High field ^{31}P (146 MHz), ^{13}C (90 MHz) and ^{1}H (360 MHz) NMR spectra were obtained by the use of a Bruker WM360 spectrometer. ^{13}C (50 MHz) and ^{1}H (200 MHz) NMR spectra were also obtained by the use of a Bruker WP200 spectrometer or a Bruker ACE200 spectrometer. Both ^{13}C and ^{31}P NMR spectra were proton decoupled unless specified otherwise . ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield from the reference. ^{1}H and ^{13}C NMR spectra were referenced to external tetramethylsilane. Elemental analyses were by Galbraith Laboratories Knoxville, TN. Irradiations were accomplished with the use of a "Blak-Ray" ultraviolet lamp (Ultra-Violet Products, Inc., San Gabriel, CA) or a Canrad-Hanovia medium-pressure, quartz, mercury vapor lamp equipped with a water-cooled quartz immersion well. Electron-impact mass spectra (EI/MS) were obtained by means of a Kratos MS 9/50 equipment. Chemical ionization (CI) mass spectra were obtained through use of a Kratos MS-25 spectrometer. Fast Atom Bombardment (FAB) mass spectra were obtained with a Kratos MS-50 spectrometer. Molecular weights were determined with a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1037A refractive index detector and a Polymer Laboratories PL gel 10-μm column. The samples were eluted with a 0.1% by weight solution of tetra-n-butyl ammonium bromide in THF. The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene} provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Research Laboratories, Watertown, MA. UV-Visible spectra of all compounds as solutions in spectroscopic grade THF or methanol were obtained by means of a Hewlett-Packard Model HP8450A UV-Visible spectrometer. The samples were in quartz cells (1-cm path length) or on quartz plates for solid polymeric samples. Glass transition

temperatures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer-7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. Heating rates of 10-40 °C/min. under a nitrogen atmosphere were used. Sample sizes were between 10 and 30 mg.

Synthesis of $N_3P_3Cl_5(OCH_2CH_2)_2OTHP$ (2): $H(OCH_2CH_2)_2OTHP$ (1.63 g, 8.58 mmol) was added to NaH (0.34 g, 14.2 mmol) in THF (50 mL) and the mixture was stirred overnight at room temperature. This solution was added dropwise over 15 min to **1** (3.0 g, 8.58 mmol) in THF (25 mL) with stirring, followed by stirring overnight at room temperature. Trimer **2** was used directly in the synthesis of **3**. ^{31}P NMR AX_2, $\nu_A = 15.9$, $\nu_B = 23.2$ ppm, $J_{PNP} = 64$ Hz.

Synthesis of $N_3P_3(OCH_2CF_3)_5\{(OCH_2CH_2)_2OTHP\}$ (3): The above reaction mixture was cooled to -78 °C, $NaOCH_2CF_3$ {from $HOCH_2CF_3$ (5.17 g, 51.7 mmol) and sodium (1.4 g, 61 mmol) and THF (30 mL)} was added dropwise and the reaction was allowed to warm to room temperature slowly. The solvent was removed by rotary evaporation, CH_2Cl_2 (150 mL) was added, and the organic layer was washed with water (3 X 100 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica, 1:3 ether:hexane) to give trimer **3**. ^{31}P NMR ($CDCl_3$) AB_2, 17.7 ppm, m; ^1H NMR ($CDCl_3$) δ 4.6 (t, 1 H), 4.30 (m, 10 H), 4.1 (q, 2 H), 3.85 (m, 2 H), 3.75 (m, 2 H), 3.50-3.65 (m, 2 H), 1.45-1.90 (m, 6 H).

Synthesis of $N_3P_3(OCH_2CF_3)_5\{(OCH_2CH_2)_2OH\}$ (4): Trimer **3** (2.10 g, 2.56 mmol) was dissolved in 95% ethanol (50 mL), and PPTS (0.064 g, 0.25 mmol) was added and the mixture was stirred at room temperature. The solvent was removed by rotary evaporation and the volatiles removed under high vacuum. Confirmation of deprotection was accomplished by establishing the absence of the protecting group signals in the ^1H NMR spectrum. ^{31}P NMR AB_2, 19.4-21.6 ppm.

Synthesis of $N_3P_3(OCH_2CF_3)_5\{(OCH_2CH_2)_2OC(O)CH{=}CHPh\}$ (5): Trimer **4** (1.80 g, 2.45 mmol) was dissolved in anhydrous pyridine (50 mL) and PhCH=CHC(O)Cl (0.61

g, 3.68 mmol) was added and the reaction mixture stirred overnight at room temperature. The solvent was removed under vacuum, water (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 X 50 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. Column chromatography (silica, 10% EtOAc/hexane) was used to isolate pure **5**. ^{31}P NMR AB_2, 16.3-18.5 ppm; ^1H NMR ($CDCl_3$) δ 7.7 (d, 1 H, J = 16 Hz), 7.5 (m, 2 H), 7.4 (m, 3 H), 6.5 (d, 1 H, J = 16 Hz), 4.2-4.4 (m, 12 H), 4.1 (m, 2 H), 3.8 (m, 4 H). MS *m/z* calcd 865, found, 866 (MH^+, +FAB).

Synthesis of $N_3P_3Cl_5\{OC_6H_4p\text{-}OBz\}$ (6): Solid HOC_6H_4p-OBz (1.55 g., 7.75 mmol) was added to NaH (0.182 g, 7.6 mmol) in THF (60 mL) and the mixture was stirred for three hours. This solution was added to $[NPCl_2]_3$ in THF (25 mL) and the mixture was stirred warm overnight. The solvent was removed by rotary evaporation, ether (50 mL) was added, and the solution was washed with water (3 X 30 mL), dried ($MgSO_4$) and the solvent removed by rotary evaporation. Warming under vacuum removed residual $[NPCl_2]_3$. Yield: 3.08 g. (78%). ^{31}P NMR AX_2, υ_A = 13.8 ppm, υ_B = 23.2 ppm, J_{AB} = 59 Hz; ^1H NMR ($CDCl_3$) δ 7.4, (m, 5 H), 7.2, (d, 2 H), 6.9, (d, 2 H), 5.05 (s, 2 H). MS, *m/z* calcd 509, found, 512 (CI), $(M+2)H^+$.

Synthesis of $N_3P_3(OCH_2CF_3)_5\{OC_6H_4\text{-}p\text{-}OBz\}$ (7): 2,2,2-Trifluoroethanol (4.80 g., 48 mmol) was added to sodium metal (1.10 g, 48 mmol) in THF (40 mL) and the mixture was stirred overnight at room temperature. This solution was added over one hour to a solution of **6** in THF (25 mL) at -78 °C and was then allowed to warm slowly to room temperature before being stirred overnight at room temperature. The solvent was removed by rotary evaporation, the solids were dissolved in ether (100 mL) and washed with water (3 X 50 mL). The organic layer was dried ($MgSO_4$) and the solvent removed by rotary evaporation. The beige solid was purified by removing $[NP(OCH_2CF_3)_2]_3$ by vacuum distillation. MS, *m/z* calcd 829, *m/z* found 830 (MH^+, CI). ^1H NMR ($CDCl_3$) δ 7.4 (m, 5 H), 7.1 (d, 2 H), 6.9 (d, 2 H), 5.0 (s, 2 H), 4.4 (q, 2 H), 4.35 (m, 4 H), 3.8 (m ,4 H); ^{31}P NMR ($CDCl_3$) AB_2, ν_A = 18.0, ν_B = 14.9 ppm, J_{PNP} = 90 Hz.

Synthesis of $N_3P_3(OCH_2CF_3)_5\{OC_6H_4p\text{-}OH\}$ (8): A solution of 7 (0.50 g, 0.30 mmol) in CH_2Cl_2 (30 mL) and $(CH_3)_3SiI$ (0.36 g,1.80 mmol, 3 equiv.) was heated to reflux for eight days. The reaction was allowed to cool to room temperature and methanol (2 mL) was added slowly. The solvent was removed by rotary evaporation and the solid purified by column chromatography (silica, 2:3 EtOAc:hexane). ^{31}P NMR ($CDCl_3$) AB_2, ν_A = 14.4, ν_B = 17.5 ppm; ^1H NMR ($CDCl_3$) δ 7.1 (d, 2 H), 6.8 (d, 2 H), 4.4 (q, 2 H), 4.2 (m, 4 H), 3.85 (m, 4 H). MS, *m/z* calcd 739, *m/z* found 740 (MH+), (+FAB).

Synthesis of $N_3P_3(OCH_2CF_3)_5\{OC_6H_4p\text{-}OC(O)CH{=}CHPh\}$ (9): A solution of trimer **8** (0.18 g, 0.24 mmol) and PhCH=CHC(O)Cl (0.018 g., 0.48 mmol) in pyridine (20 mL) was stirred at room temperature for four days. The solvent was removed under vacuum and the product was purified by preparative TLC (1:4 EtOAc:hexane). Further purification to remove $N_3P_3(OCH_2CF_3)_4\{OC_6H_4p\text{-}OC(O)CH{=}CHPh\}_2$ was not possible. MS, *m/z* calcd 869, *m/z* found 870 (+FAB, MH+).

Synthesis of $[NP(OC_6H_4p\text{-}OBz)_2]_3$ (10): To a solution of $NaOC_6H_4$-p-OBz (prepared from 6.89 g, 34.4 mmol of HOC_6H_4p-OBz and NaH (0.82 g, 34.4 mmol)) in THF (100 mL) was added solid $[NPCl_2]_3$. The solution was heated to reflux overnight . The reaction mixture was allowed to cool, the solvent was removed by rotary evaporation and the residue was extracted with boiling water (4 X 250 mL). The solid was recrystallized from 1:1 THF:hexane to yield beige needles. ^{31}P NMR δ +11, s; ^1H NMR ($CDCl_3$) δ 7.35 (m, 30 H), 6.8 (m, 24 H), 4.95 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 155.7, 144.4, 128.5, 128.0, 127.4, 121.9, 115.3, 70.4. MS, *m/z* calcd 1330, *m/z* found 1331 (+FAB), (MH+).

Synthesis of $[NP(OC_6H_4p\text{-}OH)_2]_3$ (11): Trimer **10** (1.0 g, 0.75 mmol) was dissolved in CH_2Cl_2 (30 mL) and BBr_3 (6.0 mL of a 1M solution in CH_2Cl_2, 6 mmol) was added over 5 min with the formation of a heavy precipitate. The mixture was stirred for 30 min then methanol (10 mL) was added slowly. The solvent was removed by rotary evaporation and dried under vacuum for 24 hours and used directly in the synthesis of **12**. MS, *m/z* calcd 789, *m/z* found 790 (+FAB), (MH+).

Synthesis of $[NP(OC_6H_4p\text{-}OC(O)CH{=}CHPh)_2]_3$ (12): Trimer **11** was dissolved in anhydrous pyridine (75 mL) and PhCH=CHC(O)Cl (0.91 g, 5.5 mmol) was added and the mixture was stirred at room temperature for 5 days. Most of the solvent was removed under vacuum and water (200 mL) was added to precipitate trimer **12**. Recrystallization from THF/hexane gave a beige powder. ^1H NMR ($CDCl_3$) δ 7.84 (d, 6 H, *J* = 16 Hz), 7.5 (m, 12 H), 7.35 (m, 18 H), 7.05 (m, 24 H), 6.60 (d, 6 H, *J* = 16 Hz); ^{31}P NMR ($CDCl_3$) δ 9.9, s; ^{13}C NMR ($CDCl_3$) δ 165.1, 147.7, 146.5, 134.1, 131.2, 128.9, 128.2, 122.7, 121.8, 117.2. MS, *m/z* calcd 1570, *m/z* found 1571 (+FAB, MH+). Anal. Calcd for $C_{90}H_{66}N_3O_{18}P_3$: C, 68.83; H, 4.23; N, 2.68. Found, C, 67.60; H, 4.18; N, 2.23.

Synthesis of $[NP\{(OCH_2CH_2)_2OTHP\}_2]_3$ (13): $H(OCH_2CH_2)_2OTHP$ (4.36 g, 23.1 mmol) was added to NaH (60%, 0.91 g) in THF (50 mL) and the mixture was stirred overnight at room temperature. Solid $[NPCl_2]_3$ (1.0 g, 2.8 mmol) was then added and the reaction mixture was stirred at room temperature for three days at room temperature. The solvent was removed by rotary evaporation, water (100 mL) added, and the aqueous layer was extracted with CH_2Cl_2 (3 X 50 mL). The organic layer was dried ($MgSO_4$) and the solvent removed by rotary evaporation. Column chromatography (10% MeOH/$CHCl_3$) isolated pure **13**. ^{31}P NMR ($CDCl_3$) δ 18.6, s; ^1H NMR ($CDCl_3$) δ 4.6 (t, 6 H), 4.05 (m, 12 H), 3.9 (m, 12 H), 3.75-3.40 (m, 36 H), 1.9-1.45 (m, 36 H); ^{13}C NMR ($CDCl_3$) δ 98.9, 70.5, 70.0 (m), 66.6, 65.0, 62.2, 30.5, 25.4, 19.5.

Synthesis of $[NP\{(OCH_2CH_2)_2OH\}_2]_3$ (14): Trimer **13** (3.50 g, 2.75 mmol) was dissolved in methanol (100 mL) and 0.5 mL con. HCl was added, and the reaction mixture was stirred for three days at room temperature. The solvent was removed by rotary evaporation and the oil was dried overnight under high vacuum. ^{13}C NMR δ 72.3 (m), 69.3, 64.7, 60.2 (m); ^1H NMR (ace-d_6) δ 3.9 (br, 2 H), 3.6 (m, 2 H), 3.3-3.5 (m, 4 H); ^{31}P NMR δ 19.2, s.

Synthesis of $[NP\{(OCH_2CH_2)_2OC(O)CH{=}CHPh\}_2]_3$ (15): Trimer **14** (2.10 g, 2.75 mmol) and PhCH=CHC(O)Cl (3.66 g, 22.0 mmol) were dissolved in anhydrous pyridine (75 mL) and were stirred for 3 days at room temperature. The solvent was removed under vacuum,

water (100 mL) added, and the aqueous layer was extracted with CH_2Cl_2 (4 X 50 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed by rotary evaporation. The remaining oil was purified by column chromatography (5% MeOH/CH_2Cl_2, silica). ^{31}P NMR δ 18.6, s; ^1H NMR δ 7.7 (d, 1 H, J = 16 Hz), 7.5 (m, 2 H), 7.4 (m, 3 H), 6.45 (d, 1 H, J = 16 Hz), 4.35 (m, 2 H), 4.1 (br, 2 H), 3.75 (m, 6 H). MS, *m/z* calcd 1547, *m/z* found 1548 (+FAB, MH+).

Synthesis of $[NP(OCH_2CF_3)_1(OC_6H_4\text{-}p\text{-}OBz)_1]_n$ (18): Poly(dichlorophosphazene) (**16**) (5.0 g, 43 mmol) was dissolved in warm dioxane (700 mL) overnight with stirring. 2,2,2-Trifluoroethanol (4.31 g, 43.1 mmol) was added to sodium metal (1.05 g, 45.7 mmol) in dioxane (100 mL) and HOC_6H_4p-OBz (2.6 g, 13.0 mmol) was added to NaH in dioxane and stirred overnight at room temperature. The solution of 2,2,2-trifluoroethoxide was added to the polymer solution and was stirred and warmed overnight. Finally, the solution of $NaOC_6H_4$-p-OBz was added to the partially substituted polymer and the solution was heated to reflux for five days. The solvent was removed by rotary evaporation and the solution was poured slowly into water (4 L). Further purification was accomplished by additional precipitations of THF solutions into water (4X total), iPrOH (2X) and hexane (1X). Yield: 9.8 g. (66%). ^{31}P NMR δ -17.6; ^1H NMR ($CDCl_3$) δ 7.25 (5 H, br), 6.4-7.0 (4 H, br), 4.6 (br, 2 H), 3.75 (br, 2 H).

Synthesis of $[NP(OCH_2CF_3)_1(OC_6H_4p\text{-}OH)_1]_n$ (19): Polymer **18** (0.50 g, 1.46 mmol) was dissolved in dry CH_2Cl_2 (100 mL) and $(CH_3)_3SiI$ (1.46 g, 7.3 mmol) was added and the mixture was heated to reflux for 3 days. Methanol (4 mL) was added at reflux and the solvent was decanted from the precipitated polymer. Further solvent removal was achieved by vacuum drying overnight. ^1H NMR ($CDCl_3$) δ 6.9 (2 H, br), 6.6 (2 H, br), 4.1 (2 H, br).

Synthesis of $[NP(OCH_2CF_3)_1(OC_6H_4p\text{-}OC(O)CH{=}CHPh)_1]_n$ (20): Polymer **19** (0.37 g, 1.46 mmol) was dissolved in anhydrous pyridine (100 mL) and PhCH=CHC(O)Cl (0.24 g, 1.44 mmol) was added and the solution stirred overnight at room temperature. Most of the solvent was removed under vacuum and water (100 mL) was added to precipitate the polymer. Further purification was accomplished by precipitation of THF solutions of **20** into water. ^{31}P

NMR δ -17.65, br; ^{1}H NMR ($CDCl_3$) δ 8.25 (br, 1 H), 7.7 (br, 2 H), 7.4 (br, 2 H), 7.0 (br, 4 H), 6.7 (br, 2 H), 4.25 (br, 2 H). Anal. Calcd: C, 50.15; H, 3.65; N, 3.90. Cl, 0. Found: C, 50.00; H, 3.50; N, 4.42; Cl, 0.022.

Synthesis of $[NP(OCH_2CF_3)_1\{(OCH_2CH_2)_2OTHP\}_1]_n$ (22): Poly(dichlorophosphazene) (**16**) was dissolved in THF (400 mL) overnight with stirring. $H(OCH_2CH_2)_2OTHP$ (3.93 g, 20.7 mmol) was added to NaH (60%, 0.83 g) in THF (50 mL). 2,2,2-Trifluoroethanol (1.72 g, 17.2 mmol) was added to Na (0.40 g, 17.4 mmol) in THF (50 mL) and was stirred overnight at room temperature. The THF solution of $NaOCH_2CF_3$ was added to **16** and stirred warm overnight. $Na(OCH_2CH_2)_2OTHP$ was added to the polymer solution and stirred warm for 2 days. The solution was concentrated by rotary evaporation and the polymer precipitated by pouring into water. Two additional precipitations from THF into water yielded pure **22**. Yield: 5.6 g. (98%). ^{31}P NMR δ -6.5, br; ^{1}H NMR ($CDCl_3$) δ 4.6 (br, 1 H), 4.3 (br, 2 H), 4.1 (br, 2 H), 3.8 (br, 4 H), 3.7-3.4 (br, 4 H), 1.9-1.0 (br, 6 H).

Synthesis of $[NP(OCH_2CF_3)_1\{(OCH_2CH_2)_2OH\}_1]_n$ (23): Polymer **22** (2.0 g, 6.0 mmol) was dissolved in ethanol (100 mL), PPTS (1.50 g, 6.0 mmol) was added and the reaction stirred warm for 5 days. Dialysis against water (8d) then methanol (7d), rotary evaporation of the solvent and then vacuum drying yielded pure **23**. ^{31}P NMR δ -4.9, -6.3; ^{1}H NMR: 4.5 (2 H, br), 4.2 (br, 2 H), 4.0-3.5 (br, 6 H), 2.85 (br, 1 H).

Synthesis of $[NP(OCH_2CF_3)_1\{(OCH_2CH_2)_2OC(O)CH{=}CHPh\}_1]_n$ (24): Polymer **24** was prepared by the same method as described for **20**, with the reagents and quantities as follows. **23**: 1.2 g, 4.8 mmol. Pyridine: 75 mL. PhCH=CHC(O)Cl: 0.96 g, 5.8 mmol. ^{31}P NMR δ -6.1, -7.3; ^{1}H NMR δ 7.65 (d, 1 H, J = 14 Hz), 7.5-7.3 (br, 5 H), 6.41 (d, 1 H, J = 17 Hz), 4.3 (br, 4 H), 4.1 (br, 2 H), 3.7 (br, 4 H). Anal. Calcd: C, 47.5; H, 4.52; N, 3.69. Found: C, 47.05; H, 4.93; N, 3.59. T_g: -25 °C. $M_w = 1.8 \times 10^5$, $M_n = 6.6 \times 10^5$.

Synthesis of $[NP\{O(CH_2CH_2O)_2THP\}_2]_n$ (25): Polymer **24** was prepared by the same method as described for **20**, with the reagents and quantities as follows. **16**: 3.0 g, 26 mmol in THF (500 mL). $HO(CH_2CH_2O)_2THP$: 14.7 g, 77.6 mmol. NaH: 2.79 g, 69.8 mmol

(60% dispersion in mineral oil) in THF (100 mL). ^{31}P NMR δ -7.87; ^{1}H NMR δ 4.6 (br, 1 H), 4.1-3.3 (br, 10 H), 1.7-1.0 (br, 6 H). ^{13}C NMR δ 98.8, 66.6, 65.0, 62.0, 30.6, 25.5, 19.5.

Synthesis of $[NP\{O(CH_2CH_2O)_2H\}_2]_n$ (26): Polymer **26** was prepared by the same method as described for **23**, with the reagents and quantities as follows. **25**: 1.2 g, 2.8 mmol. 95% EtOH: 100 mL. PPTS: 0.07 g, 0.28 mmol. ^{31}P NMR δ -7.98; ^{1}H NMR δ 4.16 (br, 1 H), 3.73-3.56 (m, 8 H); ^{13}C NMR δ 74.3, 73.0, 67.3, 63.0.

Synthesis of $[NP\{O(CH_2CH_2O)_2C(O)CH=CHPh\}_2]_n$ (27): Polymer **27** was prepared by the same method as described for **20**, with the reagents and quantities as follows. Polymer **26**: 2.4 g, 9.4 mmol. Pyridine: 75 mL. PhCH=CHC(O)Cl: 3.14 g, 18.9 mmol. ^{1}H NMR δ 7.6 (d, 1 H, J = 16 Hz), 7.4 (br, 2 H), 7.25 (br, 3 H), 6.4 (d, 1 H, J = 16 Hz), 4.3 (br, 4 H), 4.1 (br, 2 H), 3.7 (br, 4 H); ^{31}P NMR ($CDCl_3$) δ -7.4, s; ^{13}C NMR ($CDCl_3$) δ 166.8, 145.0, 134.3, 130.2, 128.8, 128.2, 117.8, 70.3, 69.0, 65.1, 63.5. T_g: -16 °C. Anal. Calcd: C, 58.65; H, 6.15; N, 2.85. Cl, 0. Found: C, 59.35; H, 6.15; N, 2.46; Cl, <0.5. $M_w = 5.6 \times 10^4$, $M_n = 1.4 \times 10^5$.

Synthesis of $[NP(OC_6H_4p\text{-}OBz)_2]_n$ (28): Polymer **28** was prepared by the same method as described for **18**, with the reagents and quantities as follows. **16**: 2.0 g. 1.7 mmol. Dioxane: 400 mL. HOC_6H_4p-OBz: 12.7 g, 6.4 mmol. NaH (60% dispersion in mineral oil): 1.52 g, all in dioxane (100 mL). Yield: 4.6 g. (65%).

Synthesis of $[NP(OC_6H_4p\text{-}OH)_2]_n$ (29): Polymer **28** (0.50 g, 1.13 mmol) was dissolved in dry CH_2Cl_2 (100 mL) overnight with stirring. BBr_3 (2.7 mL, 1M in CH_2Cl_2) was added and the reaction was stirred for 5 min. at room temperature. Ethanol (3 mL) was added slowly, the solvent was decanted from the polymeric precipitate, and the polymer was dried under vacuum overnight. ^{31}P NMR δ -16.1; ^{13}C NMR (DMSO-d_6) δ 153.5, 121.6, 115.0, 95.4; ^{1}H NMR (DMSO-d_6) δ 6.64 (br, 2 H), 6.31 (br, 2 H).

Synthesis of $[NP(OC_6H_4p\text{-}OC(O)CH=CHPh)_2]_n$ (30): Polymer **30** was prepared by the same method as described for **20**, with the reagents and quantities as follows. **29**: 0.29 g, 1.10 mmol. Pyridine: 75 mL. PhCH=CHC(O)Cl: 0.44 g, 2.64 mmol. ^{31}P NMR δ -16.8, br;

^{1}H NMR δ 6.4-7.6, br. Anal. Calcd: C, 68.83; H, 4.24; N, 2.68; Cl, 0. Found: C, 64.31; H, 4.06; N, 3.29; Cl, 0.0299. T_g: 59 °C.

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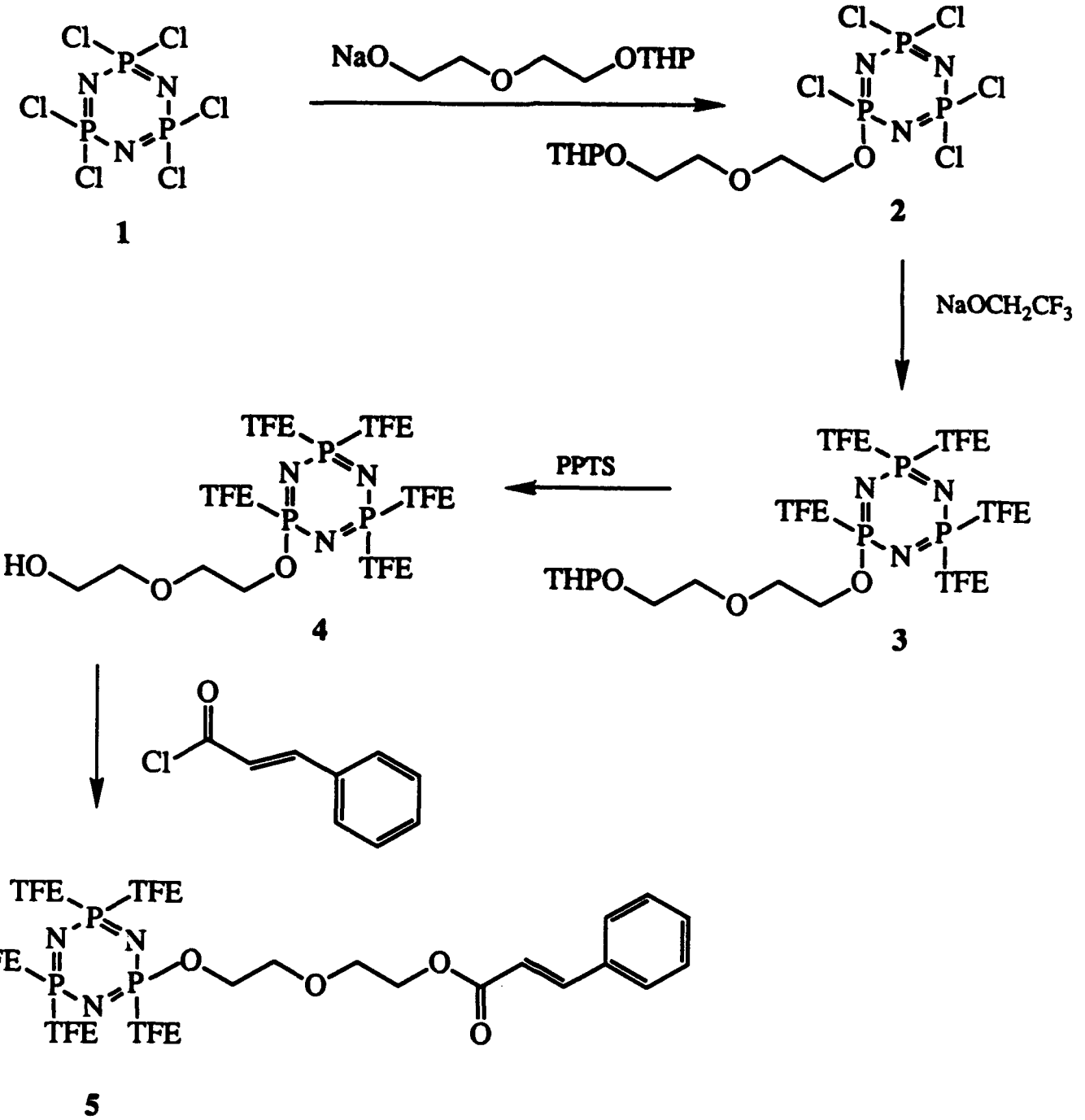
Scheme 1



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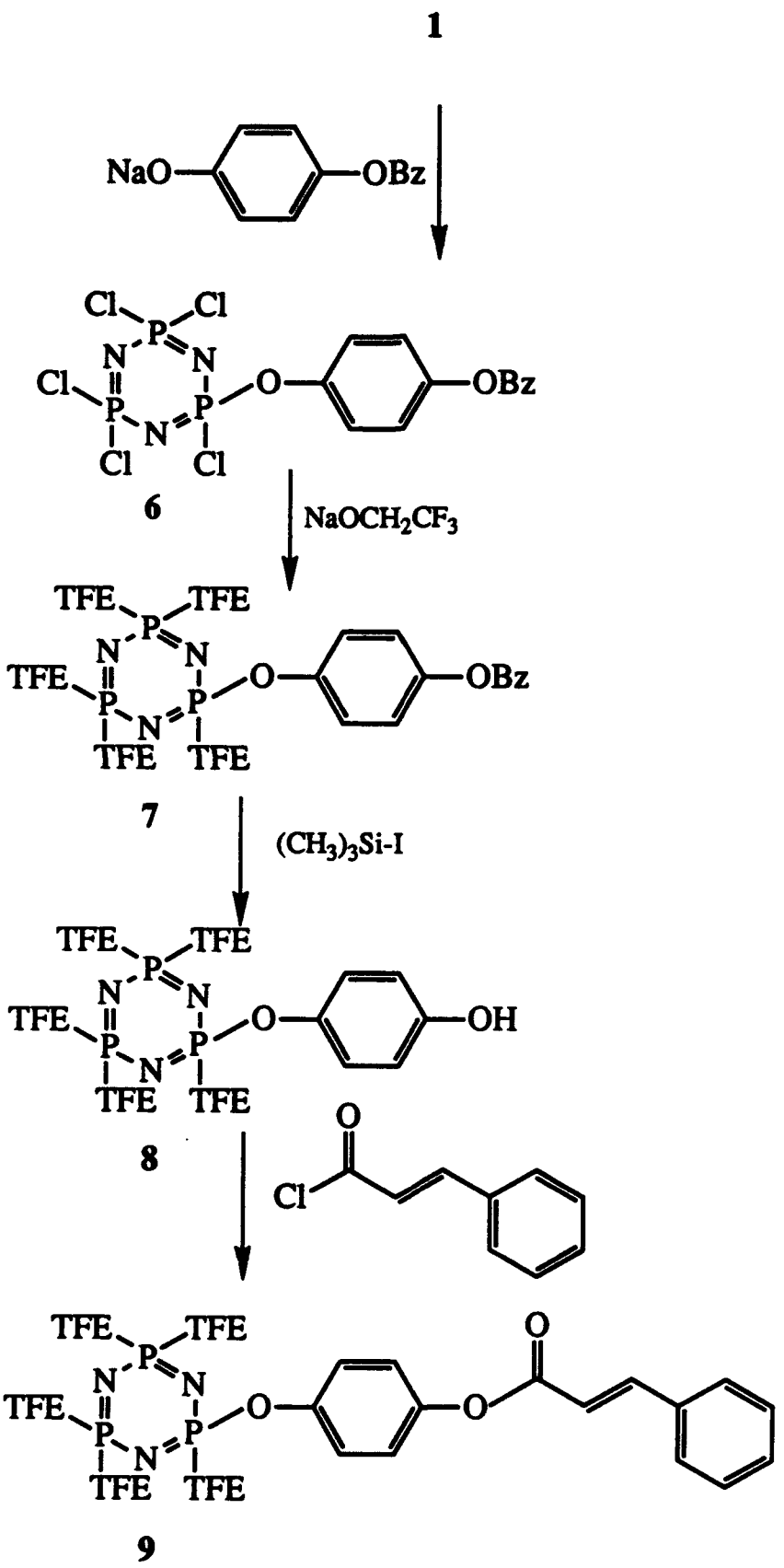

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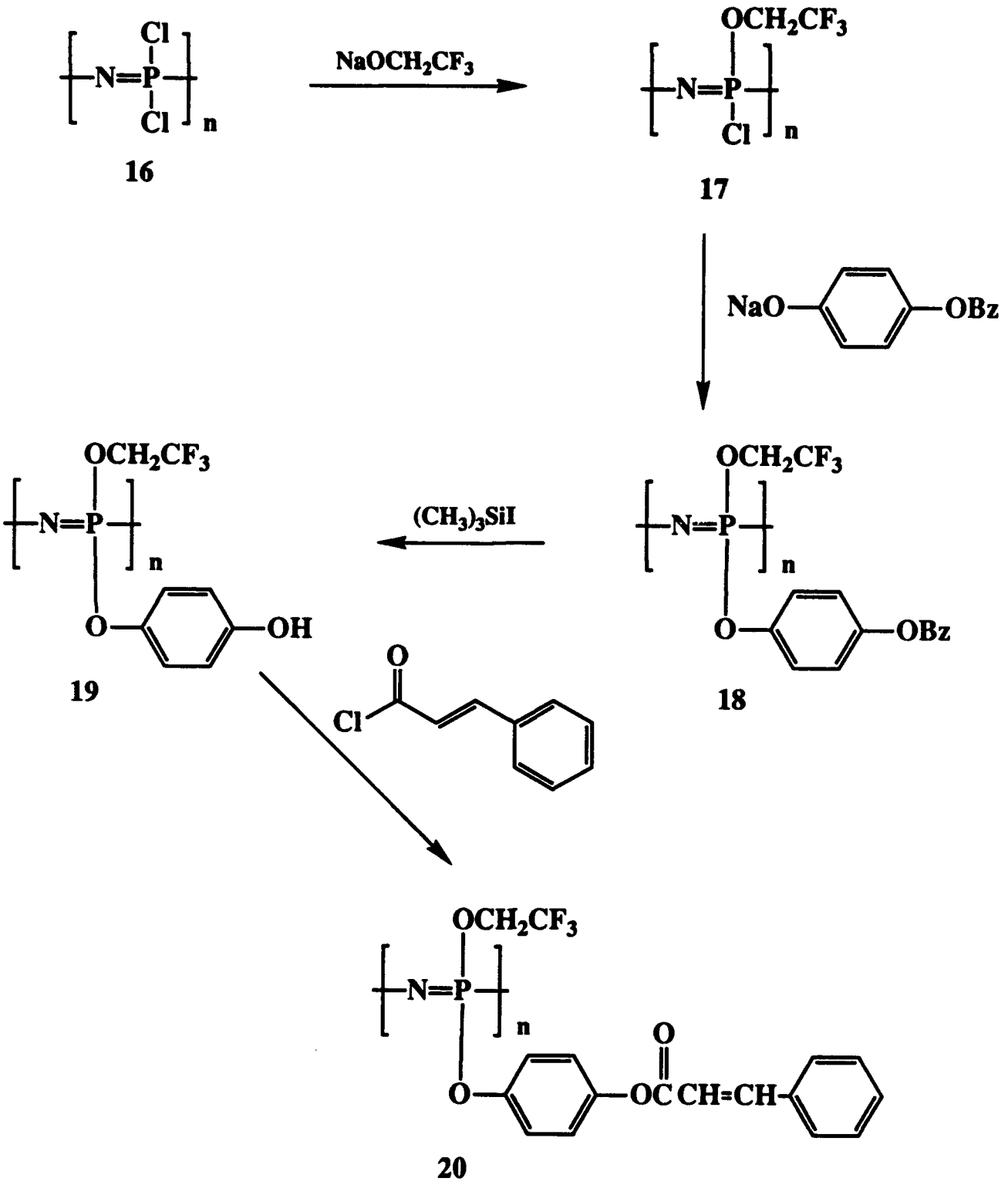
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OBz
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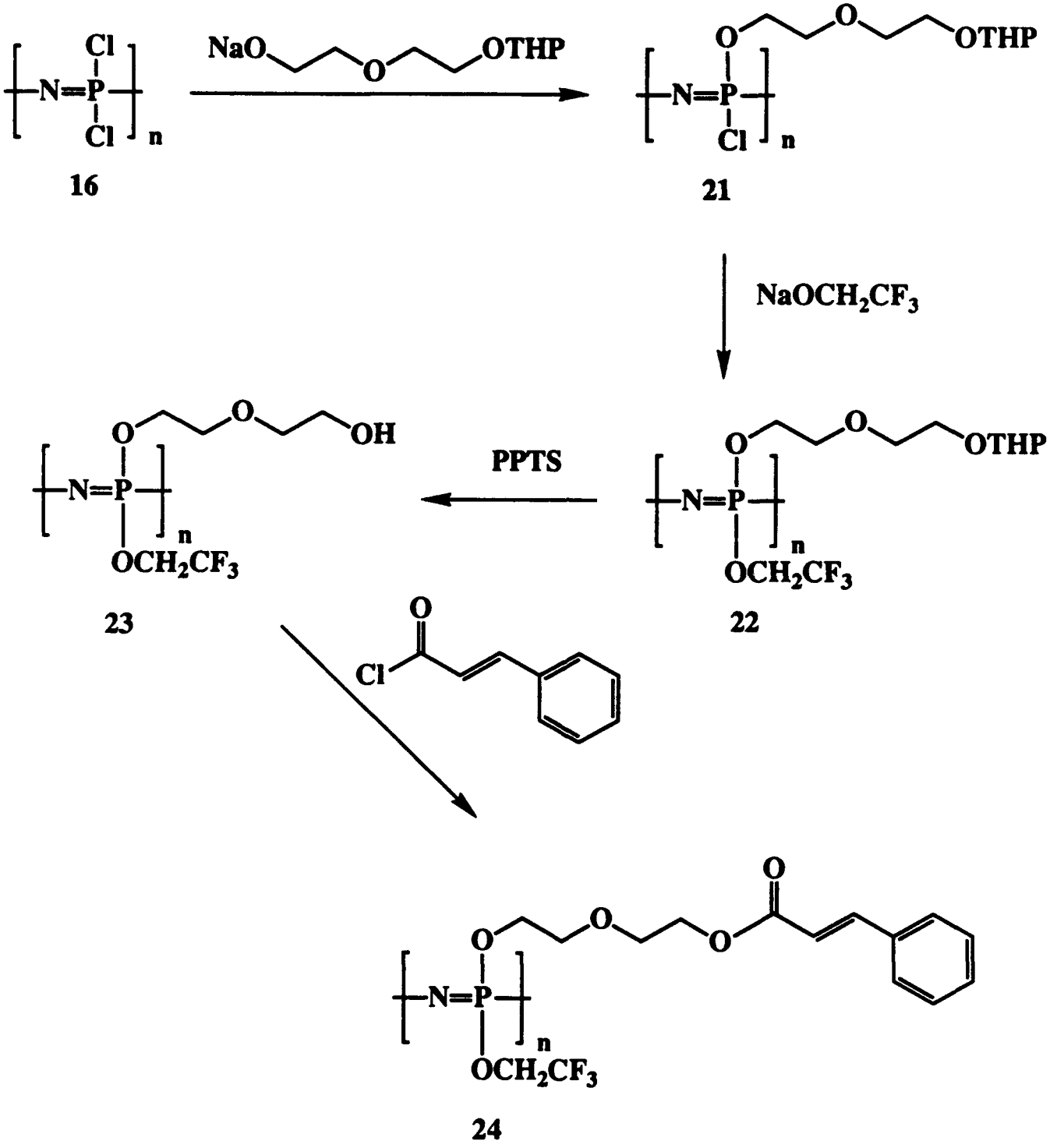
Scheme 4



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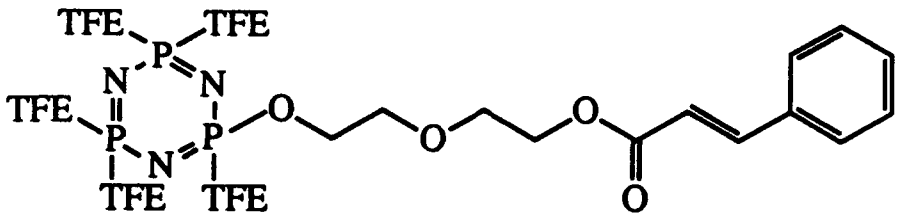

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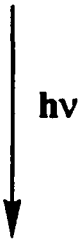

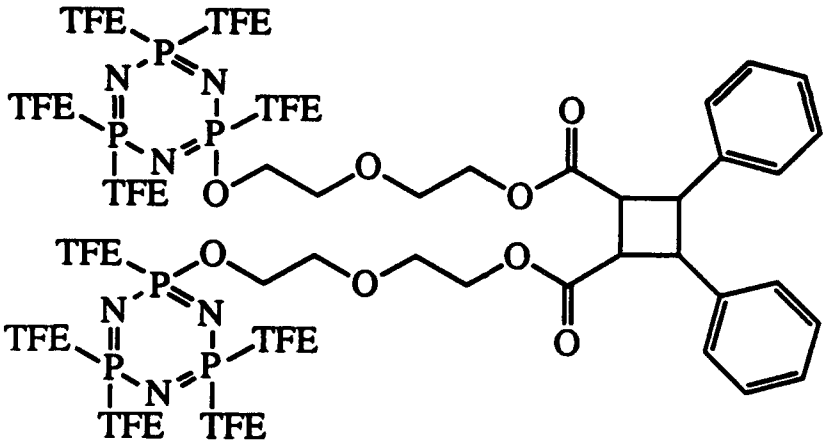

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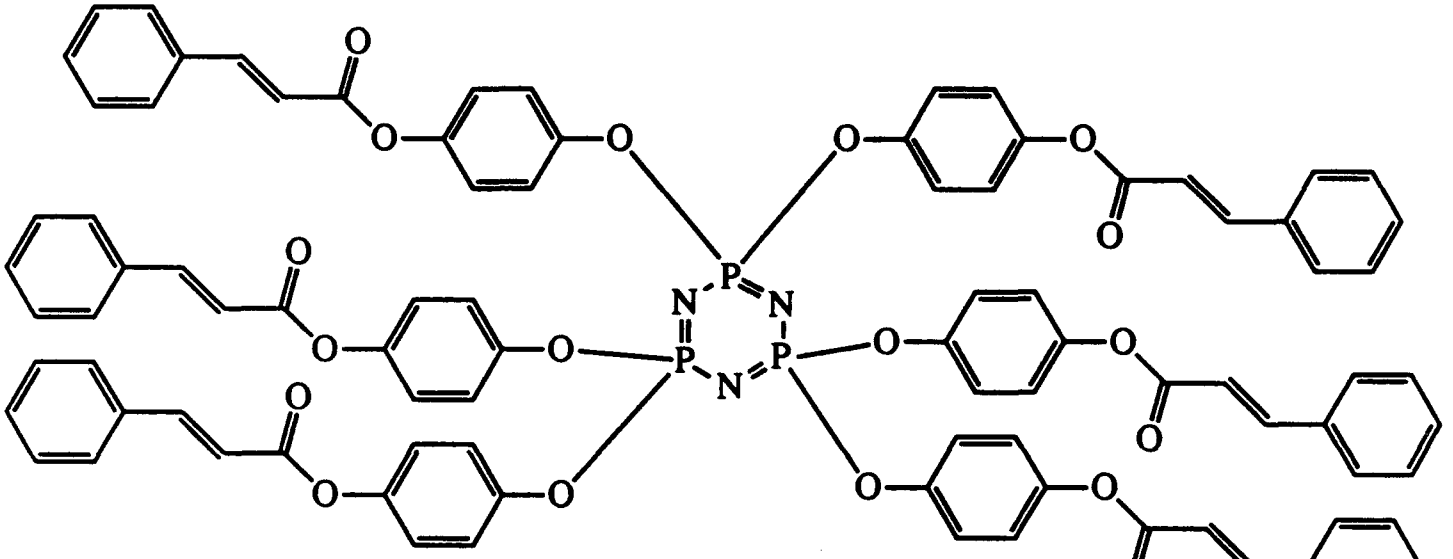

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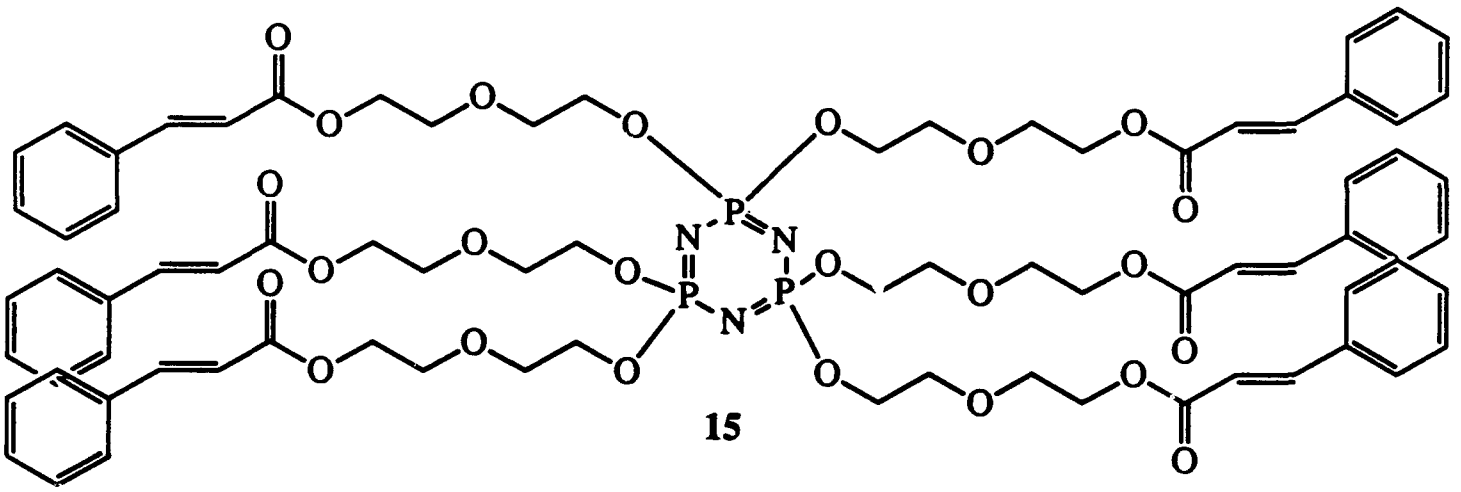

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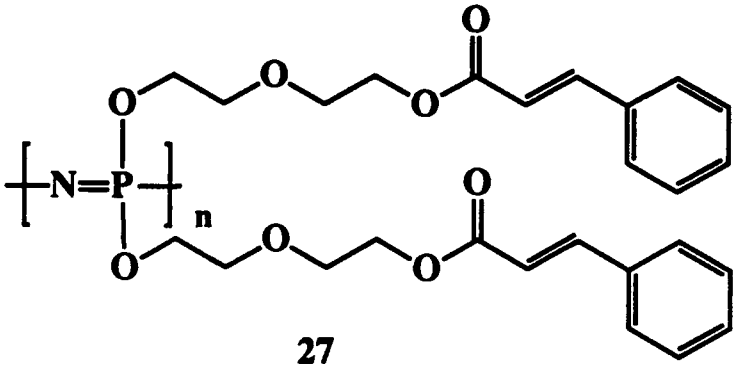

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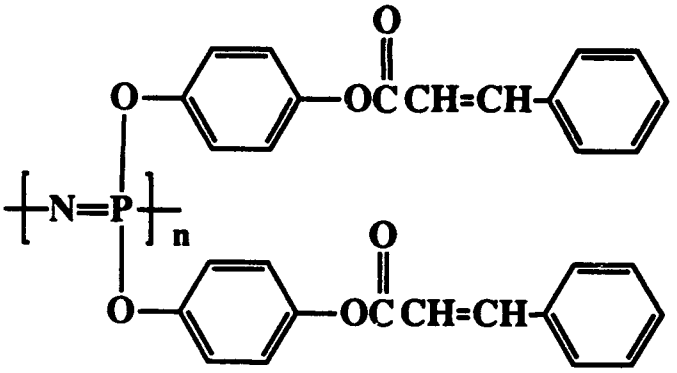
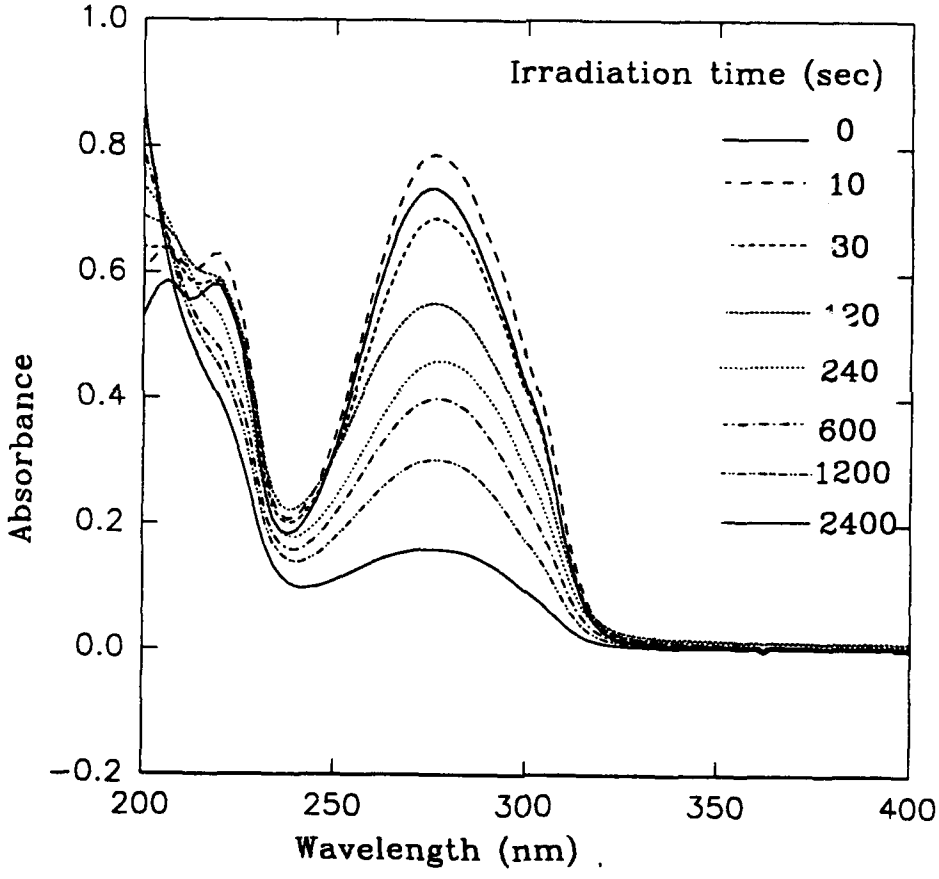


30

Figure 1: The effect of UV irradiation time on the UV spectrum of Polymer 27

Figure 2: The effect of UV irradiation time on the UV spectrum of Polymer 30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240
600
1200
2400
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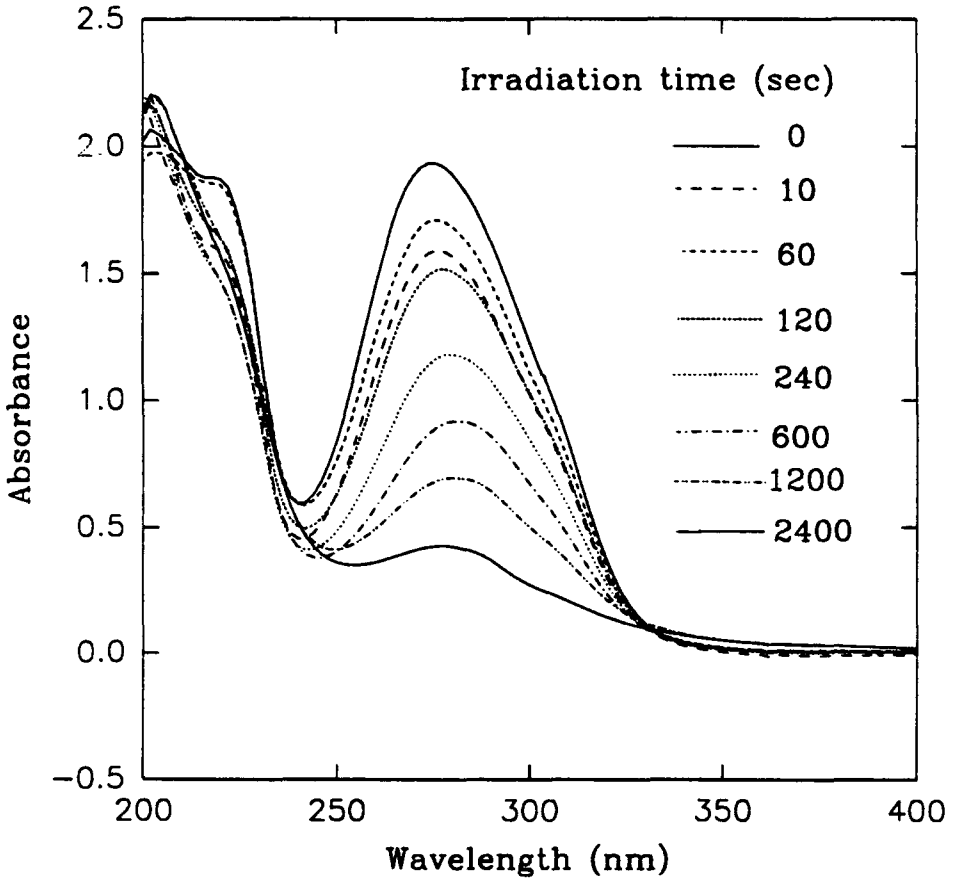
200
250
300
350
400
Wavelength (nm)

Figure 1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Wavelength (nm)
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1.0
0.5
0.0
−0.5
200
250
300
350
400

Figure 2

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